PROJECT OBJECTIVES: I) To collect samples of gas hydrate for (a) geochemical analyses, (b) phase equilibrium experiments, and (c) for solid-state NMR analysis. 2) To measure the thermal profile of the sediment column around gas vents where hydrate is forming and around brine vents where there is gas venting (but no evident hydrate formation). 3) To measure the flux of gas from gas vents where hydrate is forming and around brine vents where there is gas venting (but no evident hydrate formation). 4) To collect samples of the source gas from gas vents where hydrate is forming and around brine vents where there is gas venting (but no evident hydrate formation). 5) To document the physical size and disposition of outcropping hydrates for comparison with future observations.

RESEARCH SUMMARY: Submersible tasks that address the major objectives include: I) hydrate collections - standard push cores and a specially designed hydrate corer that can be returned to the surface under ambient pressure; 2) thermal profiles - eight thermistor recording probes built with previous NURP support and deployed from NR-I in 1994; 3) gas flux - gas flux measurement/collection device (bubbleometer) built with previous NURP support and deployed using NR-I and JSL; 4) gas samples - bubbleometers; 5) mapping - video and still photos, and permanent markers to permit future revisits.

RESEARCH RATIONALE: Gas hydrate is an ice like substance that forms, under pressure, at temperatures above the freezing point of water by inclusion of methane (and other gases) into a lattice of water molecules. Most often detected by seismic means as deeply buried layers in marine sediment, gas hydrate has also been collected from <5 m below the floor of the continental slope in the Gulf of Mexico. The stability of gas hydrate within predictable ranges of temperature, pressure, and chemical composition is critical for several reasons. Globally, subaquatic gas hydrate comprises a 1016 kg reservoir of organic carbon that may interact with the atmosphere to influence climate cycles. Regionally, they are potential energy resources as well as potential hazards to sea-floor structures. Laboratory observations and thermodynamic theory can be used to predict equilibrium conditions for gas hydrate stability, but corroborative field data are rare because few samples have been recovered and because collection removes gas hydrate from the conditions under which it forms. The discovery of gas hydrate that breaches the sea floor makes in situ observations possible. Almost nothing is known about the occurrence of natural hydrates that contain higher hydrocarbons. This work will follow our initial discovery of hydrate that breaches the sea floor with a detailed, scientific sample collection that includes recovery of hydrates at in-situ pressures. The data from measurements made on these hydrates has the potential to change our understanding of the role that hydrates play in the geochemical cycling of carbon. Very little is known about naturally formed gas hydrates, especially about those that contain significant amounts of C2+ hydrocarbons (Sassen et al., in press; Sassen and MacDonald, in review). Our observations of hydrates outcropping at the sea floor and the results inferred from measurements of gases liberated by gas hydrates have already significantly altered the ways chemists think about hydrates (Sloan,

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1994, Personal
communication). Natural hydrates are potentially unstable reservoirs of methane and other hydrocarbon gases that
are important in the context of climatic change (Sassen and MacDonald, in preparation). Results from our previous
NURP-sponsored research have demonstrated that shallow hydrate interacts dynamically with the water column, in
the sites we propose to study and by inference elsewhere in the Gulf of Mexico, by dissociating in response to
temporary increases in bottom water temperature and by episodically breaking free from the seafloor and floating
upward through the water column (MacDonald et al. in press). Measurements on samples brought back in situ
temperatures and pressures have the potential to stimulate basic research in the fields of physical chemistry,
oceanography, and geochemistry. Additional measurement of gas flux rates, thermal profiles of the sediment column
around hydrate features, and of the growth or retreat of hydrate lobes that breach the seafloor will constrain the
conditions necessary for formation of gas hydrate.
ACCOMPLISHMENTS: Together with my co-project investigator, Dr. Roger Sassen, I planned this dive series
to maximize sampling and instrumental data collection to determine the chemical composition gas hydrate and the
conditions that influence its formation and disassociation on the continental slope of the Gulf of Mexico. Blessed by
.' excellent weather and aided by the always conscientious efforts of the Harbor Branch personnel and Mr. David
Dinsmore from UNCW/NURC, all mission objectives were met or exceeded.
We designed and successfully deployed a pressure vessel in which large amounts of hydrate can be returned to the
.surface. This unique device requires some additional refmement to optimize its effectiveness; it needs a better system
of thermal insulation to protect the sampled hydrate from dissociation in the warm surface waters. Also, physically
cutting the hydrate loose from the bottom proved much more difficult than anticipated. Experience gained during this
. cruise suggests a number of design modifications that we will implement during next year's dive series. Despite these

difficulties, several large pieces of hydrate and four discrete samples of hydrate residue-gas were collected. We also
collected supporting samples of source gas, sediments with higher hydrocarbons, and carbonates associated with the
hydrate formations.
The second thrust area for this cruise was data collection through use of in-situ instrumentation deployed or extended
time courses. Here again, we enjoyed very substantial success during this dive series. Two instruments package-a -,
bottom thermistor and a current meter--were recovered early in the cruise. These provided, respectively, a I-year I
record of the temperature in vicinity of a hydrate mound at the GC234 site, and a 34 day current record for the near- ,
bottom water column at the same location. The records from the thermistor, which was deployed during my 1994 J
NURC program, demonstrate significant episodes of warming in the bottom waters over a time scale

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of weeks--as
~well as diel oscillation in temperature. Happily, the current meter deployment bracketed one such episode and will be
invaluable in determining the causes of this temperature variation. Bottom temperatures have the potential to ,
influence hydrate formation; therefore, we designed a time-lapse camera and a gas flow meter (bubblometer), both ~
equipped with recording thermistors, to monitor conditions of hydrates and gas seeps in the coming year. Both these
Idevices were successfully deployed at the Bush Hill site. They will be retrieved in the 1996 program.
BENEFITS: The data sets we collected during this cruise will form the basis of a series of papers on gas hydrate
Igeochemistry, geology, and ecology, as well as on other topics. The topics of these papers and the journals to which
we will submit them are as follows: 1
Clathrate geochemistry in marine hydrocarbon seeps: Gulf of Mexico continental slope. AAPG Bull. I
Hydrocarbon fractionation caused by hydrate formation at depth in the ocean. argo Geochem.
Episodicity in hydrate formation and dissociation determined by sea-floor instrumentation. J. Geophys. Res. Oceans ~
Large-scale spatial pattern in chemosynthetic communities. Marine Ecol. Prog. Ser.
Isotropic orientation of Gorgonacea in a deep marine canyon: Biological current meters. Deep Sea Res. ,
In addition to peer-reviewed journals, information and photographs collected during this dive series have been
Iaccepted for publication in National Geographic and Scientific American.
NEW TOPICS: During this cruise we discovered that we could observe the actual course of hydrate formation in
our gas collection vessels. This completely unexpected result suggests a number of highly novel and significant
Iexperiments. We performed the preliminary experiment by allowing hydrate to form in our collection tubes and then
emptied out the remaining gas. We theorize that gas formed by the decomposition of the hydrate residue will differ in '
composition from the source gas (which we collected earlier) due to preferential incorporation of higher
hydrocarbons. Our analyses of the gas samples will test this theory. From this simple experiment, it is a short step to
bulldmg more elaborate devices to cascade gas from one chamber to another, retammg the hydrate in each for :
analysis. Such experiments potentially have great significance for understanding how hydrates form under real world ;
conditions. ,